

REACTIVE HOT MELT ADHESIVE

This application is a continuation under 35 USC Sections
5 365(c) and 120 of International Application No.
PCT/EP02/10804, filed 26 September 2002 and published 17
April 2003 as WO 03/031490, which claims priority from
German Application No. 10149142.5, filed 5 October 2001,
each of which is incorporated herein by reference in its
10 entirety.

Field of the Invention

15 The invention relates to modified, one-component, moisture-
curing polyurethane hot melt adhesives and their use for
laminating films onto plastic, wood, derived timber
products, metals, stone or similar materials.

20 Discussion of the Related Art

A colored or patterned surface film is often applied to the
surface of objects, such as e.g. window profiles, doors,
frameworks and housings of plastic, wood, derived timber
25 products, metals or similar materials in order thus on the
one hand to protect the surface of the objects against
damaging influences, such as e.g. corrosion, discoloration
by light or mechanical effects. Another reason for
application of the surface film can be to make the surface
30 of the object more appealing.

For example, if an appropriately patterned film is used,
the impression of valuable wood can be generated, even if a
material which, because of its visual appearance,
35 structure, surface or color, would not be suitable for this
use is actually used. A surface film applied in such a way
should thus protect the surface of the object from
environmental influences, such as e.g. the effects of

water, moisture, change in temperature or light, in particular sunlight, or also environmentally harmful substances in the atmosphere.

- 5 In window and door construction, profiles of plastic, in particular profiles of thermoplastic materials, such as polyvinyl chloride (PVC), polypropylene (PP) and acrylonitrile/butadiene/styrene copolymers (ABS), have found wide use, whether for complete, hollow or core
- 10 profiles, because of their ease of preparation by the extrusion process, their low costs and their good properties in use. In the case of PVC, the PVC to be used here can be either plasticized or semi-rigid or, in particular, rigid PVC. The surface films used are either
- 15 PVC films, CPL (continuous pressure laminates) and HPL (high pressure laminates) films, (printed) paper, veneer or other sheet-like structures, which as a rule have a thickness of 0.1 to 1.0 mm. For efficient production processes, a high initial adhesive strength after a very
- 20 short time with an even greater final strength of the gluing are required. These requirements are met in an excellent manner by reactive polyurethane hot melt adhesives, but pretreatment with an adhesion-promoting layer is necessary for this on many surfaces of plastics.
- 25 The application of the adhesion-promoting layer is said to allow high production rates here and nevertheless be environmentally-friendly.

The adhesion-promoting layer can be achieved here with the

30 aid of a plasma or corona pretreatment, but adhesion-promoting primer coats in the form of primers, e.g. water-based primers, such as are disclosed in DE-A-19826329, can also be applied.

- 35 An adhesion-promoting surface pretreatment of the surfaces of plastics or films of plastics can also be carried out with the aid of the cleaning composition described in

WO 99/46352. In this case, the cleaned surfaces of plastics can also be subjected to a further mechanical, physical, chemical or electrochemical pretreatment before the gluing. This can be, in particular, application of an
5 adhesion promoter or primer, e.g. of the abovementioned type, or a pretreatment by flaming or by a corona treatment can be carried out.

For many gluings of surface films with the abovementioned
10 substrates of plastics, derived timber products or aluminum materials, completely satisfactory results are achieved.

In the field of exterior applications, newer films which are particularly resistant to weathering and light-stable
15 are increasingly being proposed. These are, in particular, films based on (meth)acrylates, in particular mixtures of various polymethacrylate homo- and copolymers. One advantage of the use of poly(meth)acrylate films is that films of different hardnesses (from brittle-hard to high
20 flexibility) can easily be produced by suitable choice of the comonomers. Another advantage is to be seen in the fact that the usual, highly light-fast organic pigments or also iron-, chromium- or nickel-containing pigments can be used for pigmenting such films.

25 The good resistance to weathering and UV of such poly(meth)acrylate films is known. Surface films constructed as multilayer films have recently been proposed to further improve the stability to light and weathering.
30 Thus, EP-A-343491 proposes multilayer films of a (meth)acrylate base film with a glass-clear polyacrylate top film and a further glass-clear protective film of polyvinylidene fluoride (PVDF) or polyvinyl fluoride (PVF).

35 Such 1- or multilayer surface films based on acrylates or methacrylates indeed have an excellent resistance to light and weathering, but permanent weather-resistant gluing of these films to the abovementioned materials of

thermoplastic polymers, wood, aluminum and the like was not possible with the hot melt adhesives known to date.

5 Brief Summary of the Invention

In view of the abovementioned prior art, the inventors had the object of providing one-component, moisture-curing polyurethane hot melt adhesives which are built up in
10 particular for gluing one- or multilayer surface films based on acrylate or methacrylate polymers or copolymers.

The present invention provides a one-component, moisture-curing polyurethane hot melt adhesive which comprises at
15 least one reaction product with reactive isocyanate groups which is obtained by reaction of at least one di- or polyisocyanate with one or more polyether-polyols, partly crystalline or crystalline polyester-polyols and/or low molecular weight polymers from olefinically unsaturated
20 monomers and optionally tackifying resins.

The present invention also provides the use of the abovementioned polyurethane hot melt adhesives for gluing single- or multilayer (meth)acrylate surface films to
25 substrates of thermoplastics, wood or aluminum. Thermoplastics which are employed here are, in particular, PVC, propylene, ABS, either as factory-new plastics or as recycled products or optionally mixtures of factory-new plastics and recycled products. The polyurethane hot melt
30 adhesive according to the invention is used in particular for gluing multilayer films of a base film based on pigmented (meth)acrylate polymers or (meth)acrylate copolymers and a surface film of methacrylate copolymers, polyvinylidene fluoride or polyvinyl fluoride or a
35 combination thereof.

The present invention also provides a process for laminating 1- or multilayer films of the abovementioned

type onto shaped articles of a thermoplastic, wood or aluminum, characterized by the following process steps:

- a) the surface treatment of the side of the 1- or
5 multilayer film to be glued is usually carried out by flaming, corona treatment, application of primer or pretreatment with a cleaner or by a combination of the abovementioned treatment methods,
- b) the hot melt adhesive is then applied to the surface
10 film
- c) the surface of the shaped article is optionally pretreated by application of primer, with a cleaner or by flaming or corona treatment, optionally followed by evaporation of the volatile constituents, optionally
15 with heat being supplied. The surface pretreatment of the surface of the shaped article can also consist of a combination of one or more of the abovementioned methods.
- d) the film is then joined to the shaped article, the film
20 optionally being pressed on by suitable means.

In particularly favorable cases, either the surface pretreatment of the surface film or also the pretreatment of the shaped article can be omitted.

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To achieve good wetting of the hot melt adhesive with the substrate surfaces, the film and/or shaped article can be heated before application of the adhesive or before the joining.

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Detailed Description of Certain Embodiments of the Invention

All known monomeric diisocyanates are in principle suitable
35 for the preparation of the polyurethane hot melt adhesive.

Monomeric di- or polyisocyanates in the context of this invention are those aromatic, aliphatic or cycloaliphatic diisocyanates having molecular weights of less than 500.

Examples of suitable aromatic diisocyanates are all the isomers of toluylene diisocyanate (TDI), either in the isomerically pure form or as a mixture of several isomers, naphthalene 1,5-diisocyanate (NDI), naphthalene 1,4-
5 diisocyanate (NDI), diphenylmethane 4,4'-diisocyanate (MDI), diphenylmethane 2,4'-diisocyanate and mixtures of 4,4'-diphenylmethane diisocyanate with the 2,4' isomer, xylylene diisocyanate (XDI), 4,4'-diphenyl-dimethylmethane diisocyanate, di- and tetraalkyl-diphenylmethane
10 diisocyanates, 4,4'-dibenzyl diisocyanate, 1,3-phenylene diisocyanate and 1,4-phenylene diisocyanate. Examples of suitable cycloaliphatic diisocyanates are the hydrogenation products of the abovementioned aromatic diisocyanates, such as e.g. 4,4'-dicyclohexylmethane diisocyanate (H_{12} MDI), 1-
15 isocyanatomethyl-3-isocyanato-1,5,5-trimethyl-cyclohexane (isophorone diisocyanate, IPDI), cyclohexane 1,4-diisocyanate, hydrogenated xylylene diisocyanate (H_6 XDI), 1-methyl-2,4-diisocyanato-cyclohexane, m- or p-tetramethylxylene diisocyanate (m-TMXDI, pTMXDI) and dimer
20 fatty acid diisocyanate. Examples of aliphatic diisocyanates are tetramethoxybutane 1,4-diisocyanate, butane 1,4-diisocyanate, hexane 1,6-diisocyanate (HDI), 1,6-diisocyanato-2,2,4-trimethylhexane, 1,6-diisocyanato-2,4,4-trimethylhexane, lysine diisocyanate and 1,12-
25 dodecane diisocyanate (C_{12} DI). MDI is an isocyanate which is particularly preferably used.

The polypropylene glycols or polybutylene glycols which are known per se are used here as polyether-polyols. Examples
30 are di- and/or trifunctional polypropylene glycols with two or, respectively, three hydroxyl groups per molecule in the molecular weight range from 400 to 20,000, preferably in the range from 1,000 to 6,000. Random and/or block copolymers of ethylene oxide and propylene oxide can also
35 be employed. Another group of polyethers which are preferably to be employed is the polytetramethylene glycols (polybutylene glycols, poly(oxytetramethylene) glycol, poly-THF), which are prepared e.g. by acid polymerization

of tetrahydrofuran, the molecular weight range of the polytetramethylene glycols here being between 600 and 6,000, preferably in the range from 800 to 5,000.

- 5 Preferably, at least two polyether-polyols are used, one polyether-polyol having an average molecular weight above 1,000 and one polyether-polyol having an average molecular weight below 1,000, the preferred range of the molecular weight for the latter being 400 to 800. Instead of the
10 polyether-polyols, in particular the low molecular weight polyols, alkylene diols, such as e.g. butanediol, hexanediol, octanediol, decanediol or dodecanediol, can also be used.
- 15 Suitable polyester-polyols are the crystalline or partly crystalline polyester-polyols which can be prepared by condensation of di- or tricarboxylic acids, such as e.g. adipic acid, sebacic acid, glutaric acid, azelaic acid, suberic acid, undecanedioic acid, dodecandioic acid, 3,3-
20 dimethylglutaric acid, terephthalic acid, isophthalic acid, hexahydrophthalic acid, dimer fatty acid or mixtures thereof, with low molecular weight diols or triols, such as e.g. ethylene glycol, propylene glycol, diethylene glycol, triethylene glycol, dipropylene glycol, 1,4-butanediol,
25 1,6-hexanediol, 1,8-octanediol, 1,10-decanediol, 1,12-dodecanediol, dimer fatty alcohol, glycerol, trimethylolpropane or mixtures thereof.

Other groups of polyols which may be employed according to
30 the invention are the polyesters based on ϵ -caprolactone, also called "polycaprolactones".

However, polyester-polyols of oleochemical origin can also be used. Such polyester-polyols can be prepared, for
35 example, by complete ring-opening of epoxidized triglycerides of a fat mixture which comprises at least partly olefinically unsaturated fatty acids with one or more alcohols having 1 to 12 C atoms and subsequent partial

transesterification of the triglyceride derivatives to give alkyl ester polyols having 1 to 12 C atoms in the alkyl radical. Further suitable polyols are polycarbonate-polyols and dimer-diols (product of Henkel), as well as
5 castor oil and derivatives thereof.

The molecular weights stated for the abovementioned polyether-polyols and polyester-polyols are number-average molecular weights, which as a rule are determined by
10 calculation from the hydroxyl number.

"Low molecular weight polymers from olefinically unsaturated monomers" in the context of this invention are polymers prepared from one or more comonomers chosen from
15 acrylic acid, methacrylic acid, C₁- to C₁₀-alkyl esters of acrylic acid or methacrylic acid, esters of (meth)acrylic acid with glycol ethers, such as methoxyethanol, ethoxyethanol, propoxyethanol and/or butoxyethanol, vinyl esters, such as vinyl acetate, vinyl propionate and vinyl
20 esters of highly branched monocarboxylic acids, such as e.g. versatic acid (product of Shell Chemie), vinyl ethers, fumaric acid esters, maleic acid esters, styrene, alkylstyrenes, butadiene or acrylonitrile and mixtures thereof.

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In a preferred embodiment, these low molecular weight polymers have active hydrogen groups in the form of hydroxyl groups or primary or secondary amino groups, so that these low molecular weight polymers can be co-bonded
30 chemically into the polymer matrix of the hot melt adhesive. The low molecular weight polymers are conventionally prepared by free-radical polymerization or copolymerization of the abovementioned monomers. For incorporation of the active hydrogen groups, hydroxyethyl
35 (meth)acrylate, hydroxypropyl (meth)acrylate, hydroxybutyl (meth)acrylate or esters of acrylic acid or methacrylic acid with glycol oligomers or polymers, such as e.g. di-, tri-, tetra- and/or polyethylene glycol can be

copolymerized with the abovementioned monomers. Instead of the abovementioned hydroxy-functional (meth)acrylates, the corresponding amino-functional comonomers can also be used. The molecular weight range of the low molecular weight
5 polymers from olefinically unsaturated monomers is between 10,000 and 150,000 dalton, preferably 20,000 and 80,000 dalton. The average molecular weight is determined here, as is conventional for copolymers obtained by free-radical polymerization, by a standard gel permeation chromatography
10 (GPC), the latter occasionally also being called "size exclusion chromatography" (SEC). For this, the average molecular weight is calibrated against an external polystyrene standard of certified molecular weight.

15 If OH-functional polymers are used, these should have an OH number (DIN 53783) of 0.5 to 20, preferably between 1 and 15. Particularly suitable low molecular weight polymers with active hydrogen groups are disclosed in WO 99/28363 on page 13 to 14. The disclosures of this publication and
20 corresponding United States Pat. No. 6,465,104 are each incorporated by reference herein in their entirety.

Tackifying resins which can be used are e.g. abietic acid, abietic acid esters, terpene resins, terpene-phenol resins,
25 phenol-modified styrene polymers, phenol-modified α -methylstyrene polymers or hydrocarbon resins.

In a preferred embodiment, these tackifying resins can contain active hydrogen atoms, so that these can be co-
30 incorporated into the binder matrix of the hot melt adhesive during the reaction with the di- or polyisocyanates. Concrete examples of these are hydroxy-functional esters of abietic acid or also hydroxylated terpene-phenol resins.

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In a particularly preferred embodiment, polyurethane compositions with no or a very low content of monomeric, low molecular weight diisocyanates can be employed as the

polyurethane hot melt adhesives according to the invention. Such hot melt adhesive compositions are the subject matter e.g. of WO 01/40342. The disclosures of this published application and corresponding United States Application
5 Ser. No. 10/148432 are each incorporated herein by reference in their entirety.

The hot melt adhesives according to the invention can furthermore additionally comprise stabilizers, adhesion-
10 promoting additives, fillers, pigments, plasticizers and/or catalysts.

"Stabilizers" in the context of this invention are to be understood on the one hand as stabilizers which effect
15 stability of the viscosity of the polyurethane prepolymer during preparation, storage or application. Monofunctional carboxylic acid chlorides, monofunctional highly reactive isocyanates, and also non-corrosive inorganic acids e.g. are suitable for this, examples which may be mentioned
20 being benzoyl chloride, toluenesulfonyl isocyanate, phosphoric acid or phosphorous acid. Antioxidants, UV stabilizers or hydrolysis stabilizers are furthermore to be understood as stabilizers in the context of this invention. The choice of these stabilizers depends on the one hand on
25 the main components of the composition, and on the other hand on the application conditions and the loads to be expected on the cured product. If the polyurethane prepolymer is built up predominantly from polyether units, antioxidants, optionally in combination with UV
30 stabilizers, are chiefly necessary. Examples of these are the commercially available sterically hindered phenols and/or thioethers and/or substituted benzotriazoles or the sterically hindered amines of the HALS ("hindered amine light stabilizer") type.

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If essential constituents of the polyurethane prepolymer comprise polyester units, hydrolysis stabilizers, e.g. of the carbodiimide type, can be employed.

Catalysts optionally contained in the system can accelerate, in a known manner, the formation of the polyurethane prepolymer during its preparation and/or the moisture-crosslinking after application of the adhesive. Suitable catalysts here which can be employed according to the invention are, in particular, the organotin and/or aminic catalysts mentioned in the abovementioned WO 01/40342 on page 11 to 13, in the amounts stated there.

10

In particularly preferred embodiments the polyurethane hot melt adhesives according to the invention can comprise

- 5 to 15 wt.%, preferably 8 to 12 wt.% of a diisocyanate, preferably diphenylmethane diisocyanate with
- 20 to 40 wt.%, preferably 25 to 40 wt.% of a difunctional polypropylene glycol with a molecular weight of between 2,000 and 6,000,
- 2 to 8 wt.% of a polypropylene glycol or alkylene diol with a molecular weight of between 200 and 600,
- 15 to 30 wt.%, preferably 20 to 25 wt.% of a crystalline or partly crystalline polyester-polyol,
- 10 to 35 wt.%, preferably 15 to 30 wt.% of a low molecular weight polymer of olefinically unsaturated monomers, preferably with hydroxyl groups,
- 2 to 8 wt.% of a preferably hydroxylated tackifying resin,
- 0.01 to 0.1 wt.% of an acid stabilizer of the abovementioned type.

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The sum of the abovementioned constituents here is 100 wt.%.

In principle the abovementioned reactive products can be prepared separately by reaction with the diisocyanate, and the isocyanate-functional reactants prepared separately in this way can then be mixed in the desired amount. Further possibilities for the preparation are disclosed in

WO 99/28363 on page 16 and page 17, the disclosures of each of which are incorporated herein by reference in their entirety. In a preferred embodiment, the polyurethane hot melt adhesives according to the invention are prepared in a
5 one-stage reaction, or if functional low molecular weight polymers are used, the total amount of the low molecular weight polymer is mixed into a small amount of one or more of the polyols, followed by addition of the total amount of the polyisocyanate. After the end of this reaction, the
10 remaining amount of the polyols or polyol mixtures is added.

The invention is described in the following with the aid of some experiments in principle, where the choice of examples
15 is not intended to represent a limitation of the scope of the subject matter of the invention. They merely show by way of a model the mode of action of the hot melt adhesives to be used according to the invention and their advantages in the gluing of one- or multilayer surface films based on
20 acrylate or methacrylate polymers to profiles of plastics, such as are conventionally employed in window construction.

In the following examples, all the amounts stated are percentages by weight or parts by weight, unless stated
25 otherwise.

Examples

Example 1

A reactive hot melt adhesive composition with free
5 isocyanate groups was prepared from the following
constituents in a heatable stirred tank:

	Polypropylene glycol, MW 2,000, OH number 56	32.18%
	Polypropylene glycol, MW 400, OH number 260	4.87%
10	Partly crystalline polyester based on hexanediol adipate, OH number 30.5	21.46%
	Acrylic copolymer, MW 34,000, OH number 2.1	24.38%
	Hydroxylated tackifier resin, OH number 75	4.87%
	4-Toluenesulfonyl isocyanate	0.03%
15	4,4'-Diphenylmethane diisocyanate	12.21%

After the end of the reaction of the isocyanate groups with
the hydroxyl groups, the hot melt adhesive composition was
introduced in the conventional manner into containers which
20 close moisture-tight, and had the following characteristic
values:

NCO content: 1.15%; viscosity of the melt at 130°C: 17 Pa.s,
measured with a Brookfield viscometer equipped with
25 Thermosel.

For lamination of PVC window profiles, the reactive hot
melt adhesive according to example 1 was used for gluing to
a standard PVC window profile a multilayer window
30 decorative film based on a pigmented acrylic film with a
transparent, colorless acrylic/polyvinylidene fluoride
coextruded film as the surface layer. The acrylate side
was used as the gluing side of the decorative film. Gluing
was carried out on a standard profile sheathing machine of
35 the type Friz, DTC-2, the PVC profile having been
pretreated with a solvent-based primer 6-B-23 from Henkel
Dorus. The knife gap of the sheathing machine was 50 μ m,
the hot melt adhesive temperature was 130°C and the

temperature of the PVC profile was 55°C. The gluing was tested for its peel strength after 10 min, 1 h, 1 day and 7 days and after ageing (7 days, 70°C with exposure to water). The results are summarized in the following table.

5

Peel strength (N/20 mm) after:

Example	Film	Adhesive	10 min	1 h	1 d	7 d	After ageing 7d/70°C, water
2	FAST	Ex. 1	7	20	48, FT	50, FT	81, FT
3	FAST	Ex. 1	4	20	75, FT	76, FT	-
4	FAST	QR5305	5	9	42, AF-F	51, AF-F	40, AF-F
5	FAST	QR3530-24	2	8	22	46, AF-F	40, AF-F
6	MBAS 2	Ex. 1	6	16	72, FT	86, FT	67, FT
7	MBAS 2	QR5305	3	4	42	84, FT	43

QR5305 = PURMELT QR5305 adhesive, Henkel KGaA

QR3530-24 = PURMELT QR3530-24 adhesive, Henkel KGaA

10 FAST = multilayer film based on pigmented acrylic film, Renolit

MBAS 2 = standard PVC film

FT = film tears without peeling

AF-F = adhesion fracture to the film

15 no result = peels with cohesion fracture

As can be seen from the above values, the hot melt adhesive according to example 1 is superior to commercially available polyurethane hot melt adhesives (QR 5305) and
 20 commercially available acrylate-based hot melt adhesives (QR 3530 - 24) in respect of the initial peel strength and of the final peel strength, also after ageing, when the highly light-stable multilayer films based on acrylic base

films are used for the gluing. At the same time, the hot melt adhesive according to the invention according to example 1 is also suitable for gluing conventional PVC films (see example 6).

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